

Appl. No. 10/005,803
Amdt. dated 12/03/03
Reply to Office Action of 11/19/03

REMARKS/ARGUMENTS

Examiner Kin-Chan Chen thanked for thoroughly reviewing the instant application and for examining the Prior Art.

Independent claim 1 has been amended to more accurately specify the claimed invention. The matter that has been used for the amendment of claim 1 has been quoted from the existing specification of the claimed invention, mostly from the description of Figs. 5b-5d that is provided starting with the second paragraph on page 19 of the specification.

Other amendments that have been provided for the dependent claims are editorial amendments such as removing redundant descriptive matter.

No new matter has been introduced by the amendments made to the claims.

Favorable reconsideration of this application in light of the above amendments and the following remarks is respectfully

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requested. All claims are believed to be in condition for allowance.

Specification

Reconsideration of the objection to the specification is respectfully requested based on the following.

The Examiner is thanked for pointing out the discrepancy between the ABSTRACT and the matter described in the specification of the claimed invention. A new ABSTRACT has been provided, correcting the problem kindly cited by Examiner. The specification is now believed to be in allowable condition.

In addition, the specification of the claimed invention has been carefully reviewed. Instances where the term "solvent" has been used and where the claimed invention would be more clearly described by using the terminology "polymer, possibly mixed with copper oxide residue", the former term has replaced with the latter terminology. It is believed that all such occurrences have at this time been addressed, removing any ambiguity from the specification.

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In light of the foregoing response, applicant respectfully requests that the Examiner's objection to the specification be withdrawn.

Claim Rejections - 35 U.S.C. § 112

Reconsideration of the rejection of claims 1-7, 9 and 11-16 under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention is respectfully requested based on the following.

Applicant respectfully refers to an amendment that has been provided in response to a previous Office Action, for page 5, last paragraph, page 6, first paragraph, which is quoted following and which clearly describes to one skilled in the art how polymer residue is removed from exposed surfaces after an etch stop layer has been removed, as follows:

"In accordance with the objectives of the invention a new method is provided for the removal of polymer from exposed surfaces after an etch stop layer has been removed. Exposed surface are treated with a first plasma etch followed by a DI

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water rinse after which a second plasma etch of exposed surfaces

is performed. By selecting the chemistry and the conditions for the first and the second plasma etch, polymer residues and formed copper oxide residues are removed from exposed surfaces."

In addition, the specification of the claimed invention has been carefully reviewed. Instances where the term "solvent" has been used and where the claimed invention would be more clearly described by using the terminology "polymer, possibly mixed with copper oxide residue", the former term has been replaced with the latter terminology. It is believed that all such occurrences have at this time been addressed, removing any ambiguity from the specification.

In light of the foregoing response, applicant respectfully requests that the Examiner's rejection of claims 1-7, 9 and 11-16 under 35 U.S.C. 112, second paragraph, be withdrawn.

Claim rejections - 35 U.S.C. § 103(a)

Reconsideration of the rejection of claims 1-5, 12-14 and 16 under 35 U.S.C. 103(a) as being unpatentable over admitted prior art (AAPA) in view of Catabay et al. (U.S. Patent 6,503,840) is respectfully requested based on the following.

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The AAPA, as kindly cited by Examiner, shows a conventional method of creating a dual damascene opening. This in order to emphasize, as indicated on pages 12 and 13 of the specification, the negative impact that is conventionally experienced in creating a dual damascene opening, and as quoted following:

"Solvents are typically applied after etching of the etch stop layer has been completed. These solvents are applied in order to remove accumulated deposits of polymer from the surface of the underlying layer of copper and from the sidewalls of the via opening that has been created as part of the process of creating a dual damascene structure. The solvents may however become trapped inside the opening of the dual damascene structure, resulting in high contact resistance between the dual damascene structures and the underlying layer of copper with which the dual damascene makes electrical contact. The trend in the art is further to use dielectrics (for the layers of dielectric in which the dual damascene structure is created) of low dielectric constant value, this in order to improved overall device performance. Low-k dielectrics are known to be relatively porous and are therefore prone to absorb a significant amount of the solvent, further having a negative effect on the performance of the dielectric and the created device. As a further

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consideration in the application must be included the cost of the solvents that are used, which tends to be high.

The impact of removing polymers, possibly mixed with copper oxide residue, as part of the creation of dual damascene structures, can be summarized as follows:

- negative impact on contact resistance
- more difficult to apply for sub-micron openings
- degrade the performance of surrounding low-k dielectric
- high cost
- considerations of the impact of removed polymer residue, possibly mixed with copper oxide residue, on the environment."

From the above quote it is clear that the AAPA is provided in order to indicate the issue that is addressed by the claimed invention, more specifically, as indicated on page 14 of the specification and as quoted following:

"Because of the above highlighted issues that are raised by the use of solvent for the removal of polymer residues, an alternate method must be provided for the removal of these polymer residues for openings of sub-micron dimensions. The

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invention provides such a method, specifically aimed at the creation of openings having a diameter in the range of 0.13 μm or less."

This latter quote brings the claimed invention and the objectives that are provided by the claimed invention in clear focus, that is, as shown in Figs. 5a and 5b of the claimed invention:

- an opening is created through layers of dielectric material such as layers of dielectric and etch stop material
- the created opening is stopped by a layer of etch stop material, as shown in Fig. 5a
- the layer of etch stop material is (must be for reasons of contact opening performance) removed from the bottom of the created opening, as shown in Fig. 5b
- polymers, possibly mixed with copper oxide residue, (55, 53, Fig. 5b of the claimed invention) are present after the step of removing the etch stop material from the bottom of the created opening. These polymers, possibly mixed with copper oxide residue, are removed by the claimed invention by very specific processing steps provided by the claimed invention, as shown in the flowchart of Fig. 4 and further in Figs. 5c and 5d of the claimed invention.

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The method of the claimed invention is specified in detail in the claims of the instant invention, for instance claim 1 specifies a method for removal of polymer, possibly mixed with copper oxide residue, from exposed surfaces, comprising:

- creating at least one opening through at least one layer of dielectric provided over the surface of an etch stop layer
- removing the etch stop layer from the bottom surface of the at least one opening
- applying a first plasma treatment to exposed surfaces
- applying a DI water (DIW) rinse to the exposed surfaces, and
- applying a second plasma treatment to the exposed surfaces.

Catabay et al. provides for the following steps for the formation of a metal-filled opening:

- forming a composite layer of dielectric comprising 1) a barrier layer formed over an Integrated Circuit structure, 2) a layer of low-k dielectric formed over the barrier layer and 3) a capping layer formed over the low-k dielectric layer
- etching an opening through the composite layer of dielectric with the help of a there-over created photoresist mask, for this etch a gas mixture is used that includes a mild oxidizing gas

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- optionally, the exposed surfaces of the low-k dielectric

material are made more dense after which the photoresist mask is removed

- the exposed surfaces of the low-k dielectric are passivated by a low-power oxygen plasma exposure

- the exposed surfaces of the created opening are cleaned and degassified, this to remove etch residues and to remove any residues remaining from the removal of the photoresist mask

- the substrate is RF cleaned with a cleaning plasma such as an argon plasma

- a glue layer such as titanium is PVD deposited over surfaces of the etched opening

- a barrier layer such as titanium nitride is CVD formed over the glue layer, and

- the created opening is filled with a conductive filler material.

From the above abbreviated analysis of the Catabay et al. invention it is clear that Catabay et al., although Catabay et al. provides a process for forming a metal filled opening, is considerably less specific than the claimed invention, more specifically as this relates to the following aspects of the

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claimed invention, aspects that have been highlighted in the specification of the claimed invention, as follows:

Fig. 5a:

- a point of electrical contact 56, comprising copper, having been provided in the surface of layer 10
- 50, a first etch stop layer, this etch stop layer serves as the etch stop for the etch of opening 51; the preferred material of the invention for etch stop layer 50 comprises nitride, carbide and composite films such as oxide/carbide, oxide nitride and the like; Catabay et al. cite the use of a barrier material such as silicon oxide ranging in thickness from at least 50 nanometers to about 100 nanometers; the claimed invention cites for this layer being a first etch stop layer, typically created to a thickness of about 1,000 Angstrom
- 54, a second etch stop layer which protects the surface of layer 52 during the etch of opening 51, and
- 56, a point of electrical contact, comprising copper, that has been provided in the surface of layer 10.

Fig. 5b:

- first etch stop layer 50 has been removed from the bottom of opening 51

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- 53, polymer, potentially mixed with copper oxidation, has

accumulated over the bottom of the opening 51 and the surface of layer 56 of copper as a result of the etch of layer 50, and

- 55, polymer that has accumulated over the sidewalls of opening 51.

Fig. 5c:

- after the first plasma treatment of the invention followed by the DIW rinse, the polymer 55 is essentially removed from the sidewalls of opening 51; oxidation of the surface of the point of electrical contact 56, comprising copper, may also have taken place.

Fig. 5d:

- after the second plasma treatment of the invention remnants 53 of polymer and potential copper oxidation residue have been removed from the surface of point of electrical contact 56.

- a contact opening 51 has been created that provides a clean and low resistivity interface with contact point 56 while all deposits of polymer and copper oxidation residue over surfaces of opening 51 have been removed.

The invention has therefore removed the previously experienced negative effects of using a solvent to remove

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polymer and copper oxide residue from an opening after the

bottom surface of this opening has been etched so that a contact plug, created in this opening, can contact an underlying layer of copper.

Specifically, the claimed invention provides for:

- eliminating a negative impact on contact resistance as a result of polymer removal combined with copper oxide residue removal
- eliminating the high cost of removing polymer and copper oxide residue, and
- eliminated considerations of the environmental impact of using and disposing solvent for the removal of polymers, which are possibly mixed with copper oxide residue.

More specifically, Catabay et al. provide, for the passivation of exposed surfaces of the low-k dielectric material by a low power (low wattage) oxygen plasma etch ranging in power from about 200 watts to about 1000 watts.

By contrast and as specified in the independent claim 1 and the supporting claims of the instant invention, the instant invention provides for

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- applying a first plasma treatment to exposed surfaces
comprising 1) the surface of said at least one layer of dielectric and to 2) said sidewalls of said at least one opening created through said at least one layer of dielectric and to 3) said exposed surface of said at least one point of electrical contact having been provided in or on the surface of said substrate
- applying a DI water (DIW) rinse to said exposed surfaces, and
- applying a second plasma treatment to said exposed surfaces.

More specifically, amended claim 1, which specifies a method for the removal of polymer and copper oxide residues from exposed surfaces, is quoted below, underlining in this quote aspects of the claimed invention that are not provided by Catabay et al., making the claimed invention patentable over the Catabay et al, invention, as follows:

- providing a substrate, at least one copper point of electrical contact having been provided in or on the surface of said substrate
- depositing an etch stop layer over said substrate
- depositing at least one layer of dielectric over said etch stop layer

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- creating at least one opening through said at least one layer of dielectric, said at least one opening having sidewalls and a bottom surface
- removing said etch stop layer from said bottom surface of said at least one opening, exposing said at least one copper point of electrical contact, said removal of said etch stop layer causing accumulation of polymers over exposed surfaces, said polymers possibly comprising copper oxide residues
- applying a first plasma treatment to exposed surfaces, said exposed surfaces comprising the surface of said at least one layer of dielectric, further comprising said sidewalls of said at least one opening, further comprising said exposed at least one copper point of electrical contact
- applying a DI water (DIW) rinse to said exposed surfaces, said DI water rinse preferably being performed at room temperature and under atmospheric pressure, said DIW rinse combined with said first plasma treatment essentially removing said polymers from said sidewalls of said at least one opening, and
- applying a second plasma treatment to said exposed surfaces, said second plasma treatment essentially removing said polymers and said copper oxide residues from said bottom surface of said at least one opening.

The two steps of plasma treatment, which are not provided by Catabay et al., are specifically provided to:

- first remove polymers 55 from the sidewalls of opening 51, shown in the cross section of Fig. 5c, after the first plasma treatment of the invention (step 40, Fig. 4) followed by the DIW rinse (step 42, Fig. 4); potentially, polymer 53 is still present over the bottom surface of the openings 51; oxidation of the surface of the point of electrical contact 56 may also have taken place, and
- second remove polymers 53, potentially mixed with copper oxidation, from the bottom of the opening 51 and the surface of layer 56 of copper.

From the above it can be stated in summary that the claimed invention, is specifically provided for:

1. addressing issues created by the use of solvents for the removal of polymers, possibly mixed with copper oxide residue, from semiconductor surfaces
2. enabling the use of polymer removal processes without detrimental effects on exposed semiconductor surfaces

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3. improving resistive performance of via plugs by removing

contact inhibiting materials from surfaces over which contact plugs are formed, and

4. optimizing the creation of contact plugs for devices having deep sub-micron device dimensions.

Regarding claims 2-4, the two steps of plasma treatment between which a DIW rinse is applied have been specified in independent claim 1 of the claimed invention. Supporting dependent claims 2-4 are required to more specifically define the claimed invention, for instance:

- the first plasma treatment providing chemically interaction with accumulated polymer deposits, dependent claim 2
- byproducts of said first plasma treatment being water soluble, dependent claim 3, and
- the first plasma treatment not causing damage to exposed surfaces of said at least one layer of dielectric deposited over the surface of said layer of etch stop layer, dependent claim 4.

For the same reasons dependent claims 12 and 13 must be provided, specifically:

- the second plasma treatment being sensitive to removing copper oxide, dependent claim 12, and

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- second plasma treatment being sensitive to not chemically

interacting with said at least one layer of dielectric deposited over the surface of said etch stop layer, dependent claim 13.

In light of the foregoing response, applicant respectfully requests that the Examiner's rejection of claims 1-5, 12-14 and 16 under 35 U.S.C. 103(a) as being unpatentable over admitted prior art (AAPA) in view of Catabay et al. (U.S. Patent 6,503,840), be withdrawn.

Claim rejections - 35 U.S.C. § 103(a)

Reconsideration of the rejection of claims 6, 7, 9, 11 and 15 under 35 U.S.C. 103(a) as being unpatentable over admitted prior art (AAPA) in view of Catabay et al. (U.S. Patent 6,503,840) as applied to claims 1-5, 12-14 and 16 above and further in view of Zhao et al. (U.S. Patent 6,204,192) is respectfully requested based on the following.

The relative merits of the AAPA and Catabay et al. have been argued above and are enclosed as this time by reference as being equally applicable to claims 6, 7, 9, 11 and 15.

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Specifically, claim 6 provides operating conditions for a N₂/O₂ based plasma treatment, claim 7 provides operating conditions for a O₂ based plasma treatment.

Regarding claims 6 and 7, basically and as a fundamental difference between the Zhao et al. invention and the instant claimed invention, the Zhao et al. invention does not provide for the three steps that are provided by the claimed invention of applying a first plasma treatment followed by a DIW rinse followed by a second plasma treatment. That Zhao et al. may teach the equivalence between using plasma treatments in a process is therefore a moot point since neither Zlao et al. nor Catabay et al. provide for the processing steps of the invention as highlighted above and as further explained in detail above. These processing steps of the claimed invention ,as specified in detail in the claims of the instant invention, are the unique steps that are provided by the claimed invention, steps which are not provided by either Zhao et al. nor by Catabay et al. singly or in combination of these inventions.

Regarding claim 15, while Zlao et al. may teach that as hydrogen plasma is used for removing etch residues and cleaning the exposed surfaces of an opening, that does not imply or there-from cannot be drawn the conclusion that Zhao et al.

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provides for the processing steps of the claimed invention of

first applying a first plasma treatment, then applying a DIW

rinse and then applying a second plasma treatment. These steps

are unique to the claimed invention, making the claimed

invention patentable over Catabay et al. in view of Zhao et al.

More specifically, claim 16 specifies the operating conditions for a second plasma treatment, which has been specified in claim 14 as being a H₂ based plasma treatment.

Neither Zhao et al. nor Catabay et al. provide for a second plasma treatment interrupted by a DIW rinse, neither one of these invention singly or in combination can therefore be equated with the claimed invention, making the claimed invention patentable over the Zhao et al. invention and the Catabay et al. invention.

While it may be true that process parameters are commonly determined by routine experiment, the instant invention is based on such experiments and has provided, in claims 6, 7, 9 and 15, the optimum conditions to achieve best results of removing polymer residue, possibly mixed with copper oxygens, from and opening created through layers of dielectric if which layers of etch stop material are part.

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Only by providing these optimum operating conditions is the claimed invention unambiguously specified and only in this manner can the claimed invention be implemented by one skilled in the art such that the two steps of plasma treatment, combined with the provided DIW rinse, give the desired results of removal of solvents from semiconductor surfaces, of enabling the use of solvent without detrimental effects for the removal of polymers from exposed semiconductor surfaces, of improving resistive performance of via plugs by removing contact inhibiting materials from surfaces over which contact plugs are formed, and of optimizing the creation of contact plugs for devices having deep sub-micron device dimensions.

While applicant acknowledges the teachings of Catabay et al. and Zahao et al. as cited by the Examiner, and although applicant does not necessarily agree that the Examiner's arguments show sufficient and proper basis for suggestion or motivation to modify or combine Catabay et al. with Zahao et al., applicant nonetheless also asserts that there is absent within the portions of Catabay et al. and Zahao et al. or any combination thereof, as cited by the Examiner, an express or

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inherent teaching of each and every limitation within

applicant's invention as taught and claimed within the claims of the claimed invention.

In this regard, applicant claims that there is absent from the portions of Catabay et al. and Zahao et al. or any combination thereof, as cited by Examiner, a teaching of applying a first plasma treatment, followed by a DIW rinse following by a second plasma treatment.

In this regard, applicant claims that there is absent from Catabay et al. and Zahao et al., or any combination thereof, as cited by Examiner, a teaching of removing polymer residue, possibly mixed with copper oxides, supported by amended claim 1 and its dependent claims, which specify the details of how these polymers possibly mixed with copper oxides are removed, providing a process that is at significant variance with the process of Catabay et al. and Zahao et al.

The instant invention provides for:

- the removal of polymers, possibly mixed with copper oxide residue, from semiconductor surfaces

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- of enabling the removal of polymers, possibly mixed with copper oxide residue, without detrimental effects caused by the removal of polymers from exposed semiconductor surfaces
- of improving resistive performance of via plugs by removing contact inhibiting materials from surfaces over which contact plugs are formed, and
- of optimizing the creation of contact plugs for devices having deep sub-micron device dimensions.

To combine the teachings of Catabay et al. and Zahao et al. is not obvious, since there is no suggestion or motivation in the teachings of any of these patents of the present invention. The instant invention specifically provides a method for the removal of polymer, possibly mixed with copper oxide residue, from exposed surfaces.

In the context of the claimed invention provides for, and not either supported by or inferred by or referred to by Catabay et al. and Zahao et al. singly or in combination thereof, at least one point of electrical contact comprising copper in a substrate, depositing an etch stop layer over the substrate, depositing at least one layer of dielectric over the etch stop layer, creating at least one opening through the at least one

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layer of dielectric, removing the etch stop layer from the

bottom surface of the at least one opening, applying a first

plasma treatment to exposed surfaces, applying a DI water (DIW)

rinse to the exposed surfaces and applying a second plasma

treatment to the exposed surfaces.

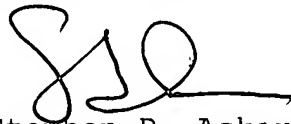
In light of the foregoing response, applicant respectfully requests that the Examiner's rejection of claims 6, 7, 9, 11 and 15 under 35 U.S.C. 103(a), be withdrawn.

Other Considerations

No new independent or dependent claims have been written as a result of this office action, no new charges are therefore incurred due to this office action.

It is requested that, should Examiner not find the claims to be allowable, to call the undersigned Attorney at the Examiner's convenience at 845-452-5863 in order to overcome any problems preventing allowance of the claims.

Respectfully submitted,



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